



Enhancement of photocatalytic H₂ evolution on pyrene-based polymer promoted by MoS₂ and visible light

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ABSTRACT

Conjugated polymers have gathered particular interests in photocatalysis because of their excellent properties such as optimization flexibility, cost-effective, and robust stability. The pyrene-based polymer (PyP), as one of the conjugated polymers, holds a great potential for water splitting because of their suitable band structure, visible light absorption, and high surface area. However, because of the fast charge carrier recombination confined by Frenkel excitons with high exciton binding energy, PyP in its pristine form remains barely active for photoctalytic hydrogen evolution. The concise construction of heterojunction is a feasible way to accelerate the charge separation, increase the lifetime of the photogenerated e⁻/h⁺ pair and decrease the activation barriers of hydrogen evolution reaction. In this work, a series of transition metal sulfides as cocatalysts have been deposited on PyP to construct heterojunctions for photocatalytic H₂ evolution reaction (HER). The loading techniques (immersion, in-situ and photodeposition) and the loading contents of cocatalysts have been investigated. The optimized MoS₂/PyP sample exhibited a 10-fold increase in comparison with pure PyP without modification. The extended π-conjugation, high surface area, and widely exposed 2D interface highlight the importance of PyP as effective supports for stabilizing the homogeneously dispersed MoS₂, thereby resulting in an efficient photocatalytic activity. This study provides a new idea to construct low-cost, sustainable and efficient hybrid system for photocatalytic hydrogen production.

1. Introduction

Photocatalytic water splitting for hydrogen production using semiconductor is an ideal potential solution to replace the traditional fossil fuels and to decrease the harmful effects of the flue gases [1–3]. With this perspective, design and synthesis of semiconductors that possess suitable band position and favorable stability for efficient water splitting is of particular importance. Recently, organic conjugated polymers (OCPs) with sufficient visible light absorption are highly concerned for photocatalytic water splitting to hydrogen; despite they are known as organic semiconductors applied to devices such as solar cells, organic LEDs, microactuators, and sensors previously [4–7].

The work of OCPs for photocatalytic water splitting can date back to 1985, while linear poly(p-phenylene)s shows H₂ evolution activity under ultraviolet light irradiation [8]. This discovery inspired the developement of conjugated polymers for photocatalytic water splitting, but their unfavorable stability and lack of visible light response extremely restrict the activity. The study on this research topic almost stops for ca. 30 years till 2009 when carbon nitride polymer

photocatalyst was discovered. Polymeric carbon nitride (PCN) is a good supplementary to the conjugated polymers' family. It exhibits robust stability and is able to capture visible photons, making it promising photocatalyst for photocatalytic water splitting [9]. Nevertheless, the photocatalytic activity of pristine PCN is still inefficient because of the fast recombination rate of the photogenerated charge carriers and absence of light absorption above 460 nm [10]. Subsequently in 2015, the fabrication of various conjugated microporous polymers (CP-CMPs) by Cooper's group with different visible light absorption and enhanced photocatalytic hydrogen activity further stimulates the development of OCPs for photocatalytic water splitting [11]. The most prominent one, pyrene-benzene polymer (named as PyP), synthesized from copolymerization of 1,4-Phenylenebisboronic acid and 1,3,6,8-tetrabromopyrene co-monomers via the typical Suzuki-Miyaura reaction. Specifically, PyP shows an excellent visible light absorption (wavelength < 520 nm) because of the narrow band gap of 2.3 eV.

Despite all of these advantages, PyP in its pristine form remains barely active for HER because of the fast charge carrier recombination, leading to low quantum yield of charge carriers arriving at the

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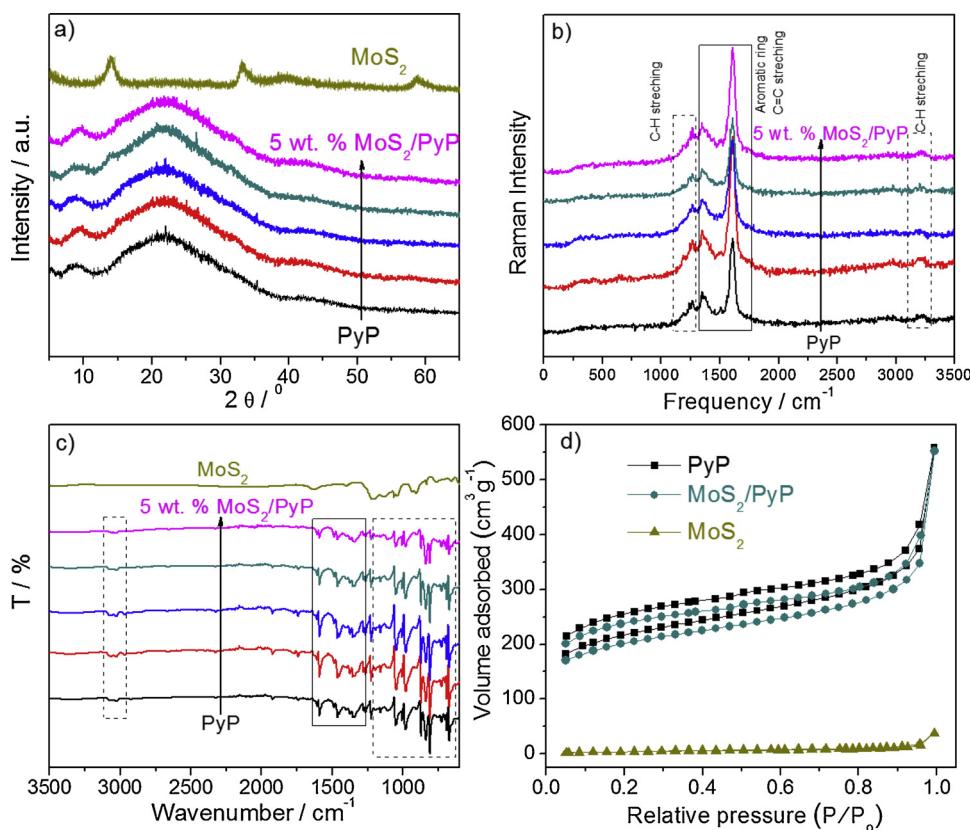


Fig. 1. (a) XRD patterns, (b) Raman spectra (c) FT-IR spectra of x wt. % MoS₂/PyP(IM) samples, (d) N₂ adsorption-desorption isotherms of pure PyP and MoS₂, and 3 wt. % MoS₂/PyP(IM) samples.

interface. One of the inherent reasons is because photoexcitation in organic semiconductors usually generates Frenkel excitons with high exciton binding energy leading to the lack of active sites on the PyP's surface [12]. Beyond that, the amorphous form of PyP means disorder in structure and abundance of defects, which also leads to the rapid charge carrier recombination making surface water reduction reactions with low activity. One can easily imagine that the activity of the polymer will be further promoted after a rational modification of the polymers.

To address these issues of OCPs, most studies are focused on designing more and more complicated new structures by organic reactions, including of poly(triazine)/heptazine-, fluorine-type, bipyridyl-, benzothiadizole-, and thiophene-based polymers [13–17]. Although molecular structure regulation of OCPs can ameliorate the high exciton binding energy or the visible light absorption, the activity of H₂ evolution is still bothered by the fast charge carrier recombination and high activation barriers [18–20]. Constructing heterojunctions is considered one of the most efficient strategies which not only enhances visible light absorption but also promotes the transfer of photogenerated charge carriers caused by their negligible overpotential and excellent kinetics [12c, 21–23]. Therefore, development of suitable materials to construct heterojunctions with PyP for photocatalytic H₂ evolution is therefore of great value. With dense active sites and an electronic conductivity, transition metals show excellent performance in photocatalytic system [24]. Among them, MoS₂ consisting of a layered S-Mo-S structure in an octahedral lattice, has been extensively investigated for electrocatalytic and powdered photocatalytic hydrogen evolution [25, 29]. Previously, MoS₂-TiO₂, MoS₂-CdS, MoS₂-RGO and MoS₂-PCN being reported mean that MoS₂ has good performance because of good electronic conductivity and offering active sites [26–29]. Moreover, the existence of π-conjugation structure in PyP, it is beneficial to interact with the lamellar structure MoS₂ to enhance the charge transfer between them and

inhibit the recombination of electrons and holes.

Herein, taking its geometrical and electronic advantages into consideration, MoS₂ is rationally loaded onto the surface of PyP to construct an organic-inorganic heterojunction for improving H₂ production activity. We expect that the distinct nanoscale structure of MoS₂ can increase the accessible area around the PyP's interface and decrease the barrier for electron transport, thus facilitating the electron transfer across the interface by the electron tunneling effect and offering more active sites. Construction of the MoS₂/PyP heterojunction was prepared via facile immersion, photodeposition and in-situ method (named as MoS₂/PyP(IM), MoS₂/PyP(PD), MoS₂/PyP(IS), where IM, PD, and IS represent the fabrication techniques). The characterization results indicate that MoS₂/PyP(IM) shows optimum photoactivity. The effect of other transition metal sulfides (FeS₂, CoS₂, NiS₂) for PyP (MS₂/PyP) were also investigated and all the as-prepared composites showed good photocatalytic H₂ production activity. Therefore, the MS₂/PyP heterojunctions is desirable as, in principle, can improve the photocatalytic hydrogen production activity. In addition, to gain further insight into the photocatalytic mechanism of the heterostructure, the photoelectrochemical properties of pure PyP and MoS₂/PyP(IM) have been further carried out. We believe that it should provide a choice to develop new materials like PyP-based photocatalysts for hydrogen evolution reaction.

2. Experimental

2.1. Preparation of PyP

A flask was charged with the monomers, 1,4-Benzene diboronic acid (3.5 mmol), 1,3,6,8-tetrabromopyrene (7.0 mmol), using Pd(PPh₃)₄ (0.8 mol%) as a catalyst in N,N-dimethylformamide (50 ml) and aqueous K₂CO₃ (2 M, 10 ml) with stirring to mix the monomers evenly.

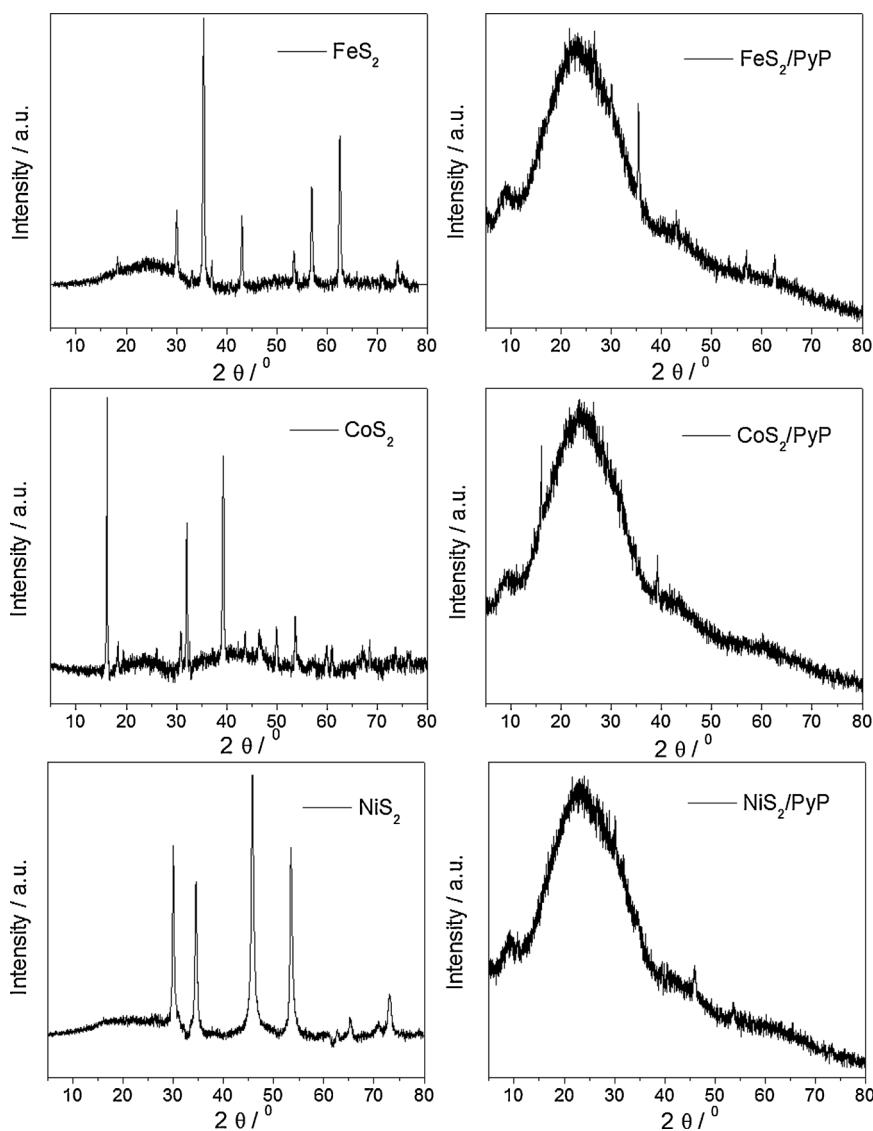


Fig. 2. XRD patterns of pure MS_2 and 3 wt. % MS_2/PyP (IM) samples.

Then the mixture was degassed by Ar for 30 min, and the reaction was carried out at 150 °C for 48 h. After work-up, the mixture was taken out and washed thoroughly with deionized water and methanol. The product was further purified by Soxhlet extraction with tetrahydrofuran for 2 days and finally dried in a vacuum oven [11].

2.2. Preparation of MoS_2

MoS_2 was prepared by typical hydrothermal method [25]. Sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) and thiourea (molar ratio = 1:2) were put into 60 mL distilled water with magnetic stirring. After completely resolved, the mixture reacted in a 100 mL Teflon-lined stainless steel autoclave at 200 °C for 12 h. After cooling, the resulting product was collected, washed with distilled water three times, and finally dried at 60 °C.

2.3. Fabrication of and MoS_2/PyP

Immersion method ($\text{MoS}_2/\text{PyP}(\text{IM})$): 0.2 g PyP was immersed into 4 mL aqueous solutions with different amounts of MoS_2 . The mixture was stirred and ultrasonication for 10 min. The final sample was obtained after evaporation and dried.

In-situ method ($\text{MoS}_2/\text{PyP}(\text{IS})$) : $\text{MoS}_2/\text{PyP}(\text{IS})$ was synthesized

under the same condition of MoS_2 with the addition of PyP in the reaction.

Photodeposition [MoS_2/PyP (PD)]: $\text{MoS}_2/\text{PyP}(\text{PD})$ samples was synthesized by photodeposition method. The precursor of MoS_2 is $(\text{NH}_4)_2\text{MoS}_4$ which was synthesized according to the literature [30]. Briefly, 1 g ammonium molybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) was added into 15 mL aqueous ammonium sulfide ($(\text{NH}_4)_2\text{S}$, ca. 20 wt. %) and stirred to react completely. And then, the-obtained red precipitate was washed with absolute ethanol and dried in the vacuum oven. For the MoS_2/PyP (PD), a certain amount of PyP was dispersed in the mixture solution ($V_{\text{ethanol}}:V_{\text{water}} = 1:4$), then $(\text{NH}_4)_2\text{MoS}_4$ was added and stirred for several hours. After being evenly dispersed, the mixture was evacuated several times; the suspension was irradiated under visible light for 1 h. After work-up, the products were filtrated and washed with deionized water several times. After drying, the $\text{MoS}_2/\text{PyP}(\text{PD})$ sample were obtained.

2.4. Fabrication of and MS_2/PyP (M is transition metal Fe, Co, Ni)

MS_2 was prepared as previously reported work [25,31]. $\text{MCl}_2 \cdot n\text{H}_2\text{O}$ (0.02 mol) and thiourea (molar ratio = 1:2) was added into aqueous ethanediamine (25 ml, 0.187 M). After fully mixed, 30 ml ethanediol was added into the solution, and stirred for 1 h. Then the mixture was

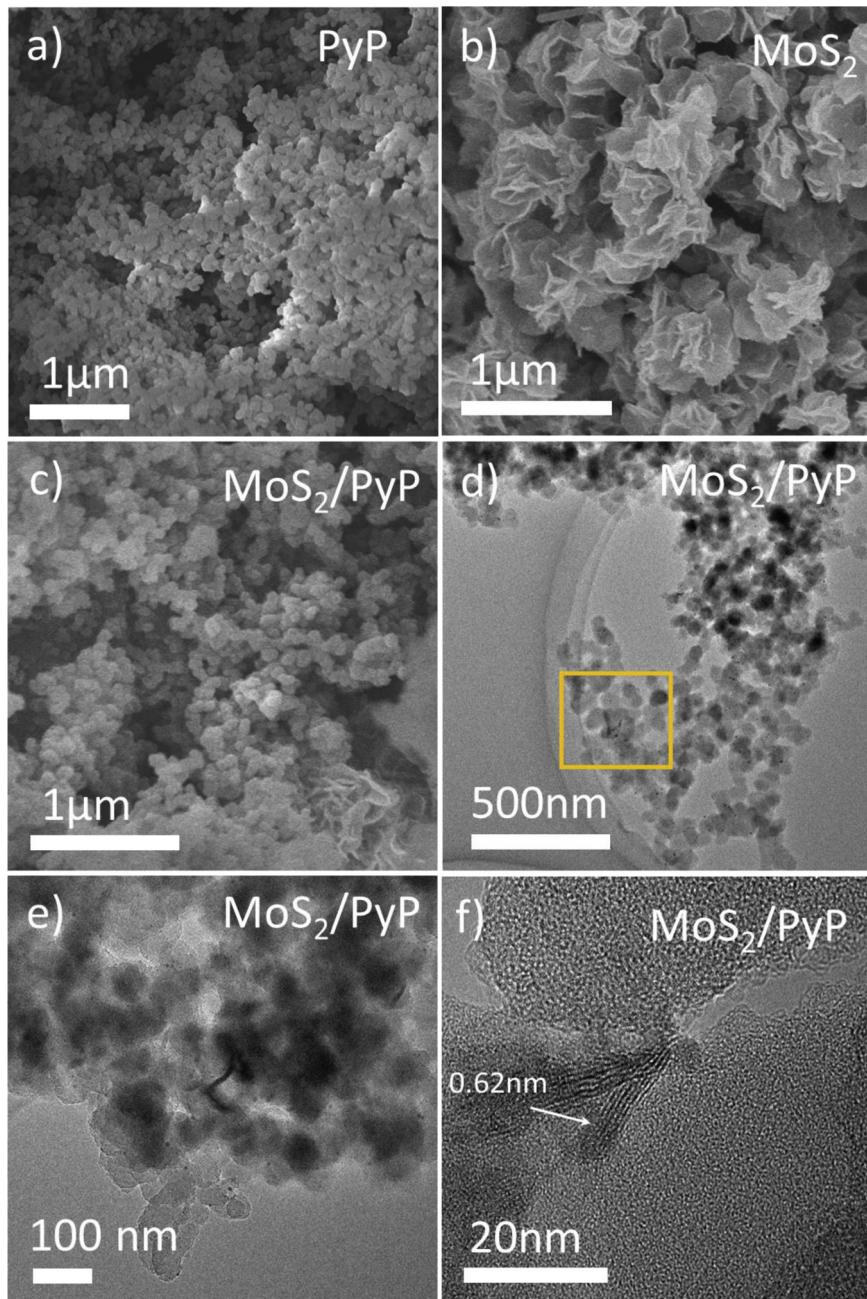


Fig. 3. SEM images of (a) pure PyP, (b) MoS₂ (c) 3 wt. % MoS₂/PyP(IM) samples; (d, e, f) TEM images of 3 wt. % MoS₂/PyP(IM) samples.

transferred to the steel autoclave and heated at 180 °C for 12 h. After cooling, the resulted participate was collected, washed with distilled water three times, and finally dried at 60 °C for overnight.

The MS₂/PyP was obtained by immersion the same with MS₂/PyP (IM).

2.5. Characterizations

The characterizations of resultant catalysts were carried out by powder XRD, XPS, TEM and FTIR to confirm the composition, structure, and textural properties. The crystal phases of samples were investigated by Powder X-ray diffraction (XRD) measurements on a Bruker D8 Advance diffractometer with Cu-K 1 radiation ($\lambda = 1.5406 \text{ \AA}$). Nitrogen adsorption-desorption isotherms were collected at 77 K using Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Raman spectra were recorded on a Laser Raman Micrometer (Invia Reflex).

Fourier transform infrared (FT-IR) spectra were recorded on a BioRad FTS 6000 spectrometer. The morphology of the sample was investigated by field emission scanning electron microscopy (SEM) (JSM-6700 F) and transmission electron microscope (TEM) (JEM 2010 EX). X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo ESCALAB250 instrument with a monochromatized Al K α line source (200 W). UV-vis diffuse reflectance spectra (DRS) were performed on a Varian Cary 500 Scan UV-vis system using BaSO₄ as the reference. Photoluminescence spectra (PL) were done on an Edinburgh FI/FSTCSPC 920 spectrophotometer. Electron paramagnetic resonance (EPR) measurements were carried out on a Bruker model A300 spectrometer. Electrochemical measurements were conducted with a BAS Epsilon Electrochemical System in a conventional three electrode cell, using a Pt plate as the counter electrode and an Ag/AgCl electrode (3 M KCl) as the reference electrode. The working electrode was prepared on fluorine-tin oxide (FTO) glass. The 5 mg sample was dispersed in 1 mL

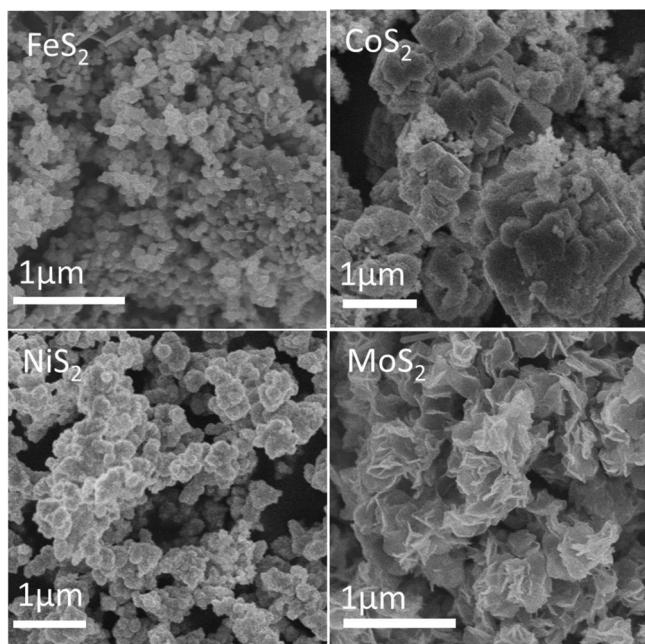


Fig. 4. SEM images of MS₂ (FeS₂, CoS₂ and NiS₂) and MoS₂ samples.

DMF by sonication. The slurry was spread onto pretreated FTO glass. After air-drying, the working electrode was further dried at 393 K for 1 h to improve adhesion. Then, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin. All the photoelectrochemical measurements were carried out in 0.2 M NaSO₄ aqueous solution, which was irradiated by simulated solar light (Shenzhen ShengKang Technology Co., Ltd, China, LX300F).

2.6. Photocatalytic test

The photocatalytic hydrogen production reaction was carried in a Pyrex top-irradiation reactor connected to a glass closed gas system at room temperature. In the photocatalytic experiment, 50 mg of catalyst powder was dispersed in an aqueous solution (100 mL) containing methanol (10 vol. %) as sacrificial electron donor. A 300 W Xeon lamp with a working current of 15 A (Shenzhen ShengKang Technology Co., Ltd, China, LX300 F) was used as a light source. The evolved gases were analyzed by gas chromatography using a thermal conductive detector (TCD).

3. Results and discussion

3.1. Photocatalyst characterization

The MoS₂ and PyP samples were characterized by X-ray diffraction (XRD) displayed in Fig. 1a. It can be observed that only broad diffraction peaks can be found in the XRD patterns of PyP, indicating that the amorphous structure of the as-prepared pyrene-based polymer. All the diffraction peaks of pure MoS₂ are termed as hexagonal structure of typical MoS₂ [JCPDS card no. 73-1508] [25b]. There are no MoS₂ signals appeared in the diffractions of x wt. % MoS₂/PyP(IM) samples because of the little loading and the weak diffraction peaks of MoS₂. All the XRD patterns of x wt. % MoS₂/PyP(IM) samples only displays one main broad peak at 21.8°. After modification with MoS₂, there are no obvious structure change can be observed. So we can conclude that deposition with MoS₂ did not alter the characteristic functional group features of PyP.

The Raman spectra (Fig. 1b) and Fourier-transform spectra (FT-IR, Fig. 1c) provide good supporting evidence for this conclusion. All Raman spectrum of x wt. % MoS₂/PyP(IM) samples displays three main

peaks: the characteristic bands of aromatic pyrene polycycles at 1620 cm⁻¹ and 1350 cm⁻¹, the C–H stretching at 1260 cm⁻¹ and 3200 cm⁻¹, respectively [32]. No evident difference in the band position of MoS₂/PyP can be viewed in comparison with pure PyP. In the FT-IR spectra of MoS₂/PyP(IM), the feature-distinctive stretch modes of aromatic ring C=C are centered at 1250 to 1620 cm⁻¹, the C–H variations are located at 650 to 1230 cm⁻¹ and 3050 cm⁻¹, which are in good accordance with pristine PyP. As shown in Fig. 1c, the characteristic peaks of MoS₂ are mainly located at ~1500 cm⁻¹, which is quite close to the aromatic ring vibrations of PyP [32c]. The vibrations of the MoS₂ are hardly observed in the MoS₂/PyP, presumably due to the overlap of the band with that of the aromatic ring vibrations. This meaning structural effect of PyP is ruled out in improving the hydrogen production performance.

The low temperature N₂ BET analysis of pure PyP and MoS₂/PyP (IM) samples was investigated. Fig. 1d shows a typical IV isotherm featuring with a pronounced H1-type hysteresis loop for polymer networks, supporting the surface area of the samples. The BET surface areas of pure PyP and MoS₂ are respectively determined as 710 and 16.5 m² g⁻¹, while that of the MoS₂/PyP(IM) samples is 658 m² g⁻¹. Compared with pure PyP, the modified sample exhibits slightly decreased specific surface area because of the mild agglomeration of PyP in the immersion.

Other transition metal sulfides (FeS₂, CoS₂ and NiS₂) obtained by similar hydrothermal were characterized by XRD patterns (Fig. 2). Obviously, the diffraction peaks belonging to pure MS₂ could be observed in the XRD patterns of MS₂/PyP(IM) which is different from that of MoS₂/PyP(IM). Maybe the reason is MS₂ with better crystallinity lead to stronger diffraction peak intensity than the former.

Field emission scanning electron microscopy (SEM) and high-resolution scanning transmission electron microscope (TEM) measurements were used to explore the morphologies of MoS₂/PyP(IM) subsequently. SEM of pure PyP (Fig. 3a) shows a small particle size almost 40–100 nm while MoS₂ nanosheets (Fig. 3b) show ~100 nm in y axis and a few nanometers in thickness. From the SEM image of MoS₂/PyP sample in Fig. 3c, MoS₂ could be distinguished from PyP because of the obvious different morphology. TEM image of the 3 wt. % MoS₂/PyP (IM) in Fig. 3d shows that MoS₂ with a typical layered structure are distributed on the surface of PyP. The high-resolution TEM (HR-TEM) image of MoS₂ displays a lattice fringe with d-spacing of 0.62 nm (Fig. 3d) corresponding to the (002) plane of hexagonal structure, which is identified with XRD pattern. All the above characterizations reveal that MoS₂ is successfully loaded on PyP using the simple synthetic approach. SEM of other transition metal sulfides (FeS₂, CoS₂ and NiS₂) shows the morphologies of MS₂ were blocky while MoS₂ are multiple layered nanoflowers (Fig. 4).

The chemical states of MoS₂/PyP(IM) were examined by X-ray photoemission spectroscopy (XPS) (Fig. 5). The binding energy at 284.6 eV is ascribed to C–C, C=C & C–H of PyP. The patterns revealed that the Mo/S atomic ratio of 1:2.09, in good agreement with the previous reports. [25] The binding energies of the Mo 3d_{5/2} and Mo 3d_{3/2} peaks located at 229.7 and 232.9 eV, S 2s band at 226.8 eV, respectively, demonstrating the values of Mo⁴⁺ and S²⁻ in MoS₂. The other two weak peaks at 234.6 and 231 eV is assigned to the value of Mo⁵⁺, presumably owing to the small amount of surface oxidation. [33] S 2p bands at 163.6 and 162.5 eV, respectively, further confirmed the dominant existence of S²⁻ [25c]. Compared to pure MoS₂, the peaks in MoS₂/PyP(IM) positively shifted with respect to the corresponding peaks because the strong interaction between PyP and MoS₂ could indirectly weaken the Mo–S bonds by decreasing the electron density around S atoms in MoS₂ [34].

The optical features of the MoS₂/PyP(IM) were assessed by UV-vis spectroscopy and photoluminescence, electron paramagnetic resonance (EPR) spectra, and electrochemical impedance spectroscopy (EIS). In Fig. 6a, as expected, the DRS spectra of MoS₂/PyP(IM) revealed a red shift in the optical absorption onset indicating broaden the light

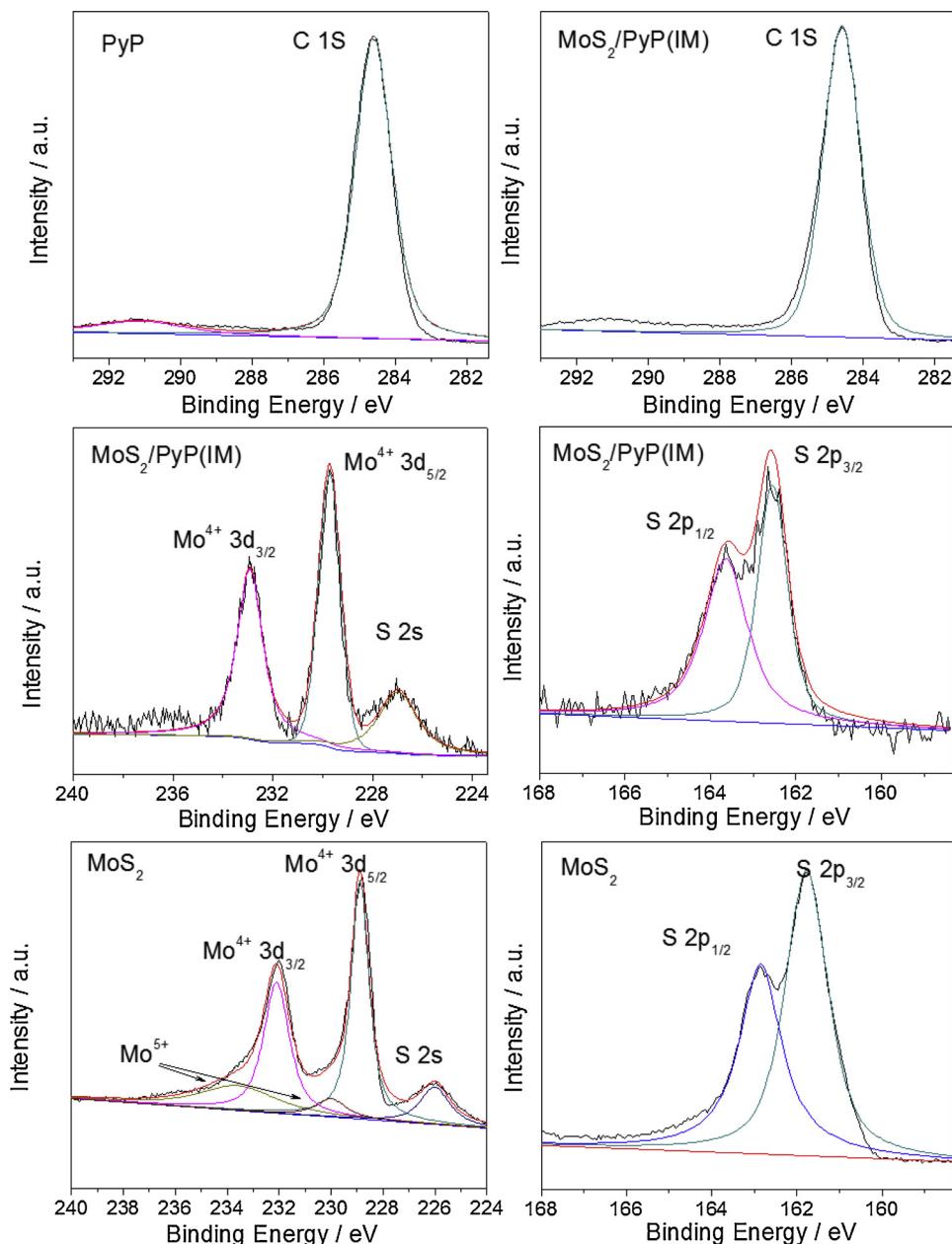


Fig. 5. High-resolution XPS spectra of C 1s, Mo 3d, and S 2p of pure PyP, MoS₂ and MoS₂/PyP(IM) samples.

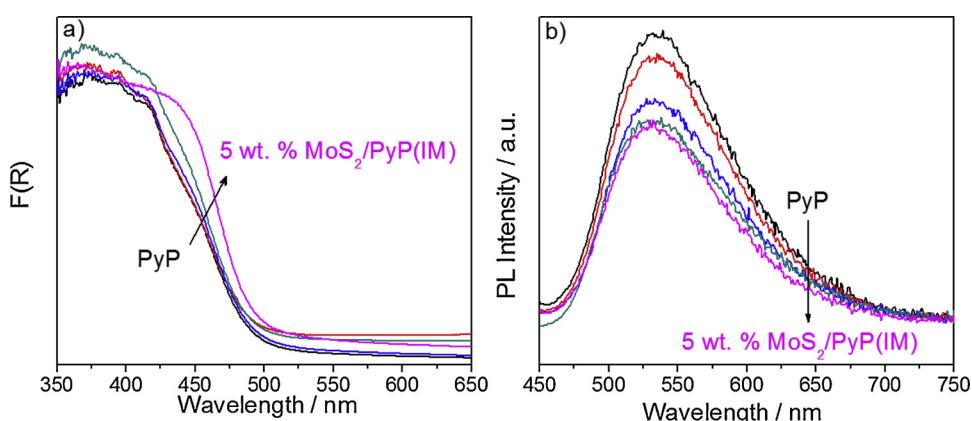


Fig. 6. Semiconductive optical features (a) UV-vis diffuse reflectance spectra, (b) PL spectra of x wt. % MoS₂/PyP(IM) samples.

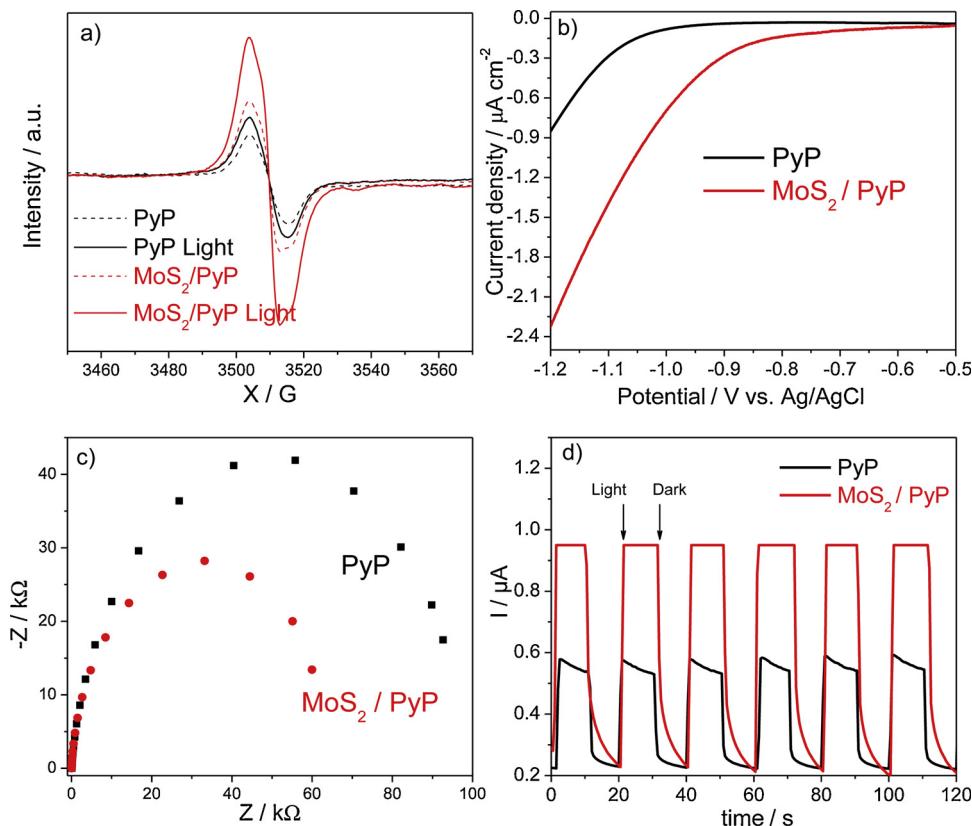
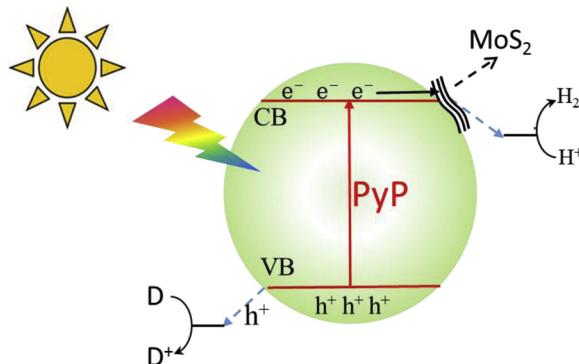


Fig. 7. a) Room temperature EPR spectra; Photoelectrochemical properties b) Polarization curves, c) Electrochemical impedance spectroscopy plots in the dark, d) Periodic on/off photocurrent response under visible-light irradiation ($\lambda > 420$ nm) at 0.4 V bias potential vs. Ag/AgCl in a 0.2 M Na₂SO₄ aqueous solution of pure PyP and 3 wt. % MoS₂/PyP(IM) samples.



Scheme 1. Schematic illustration of the between PyP and MoS₂. D = donor.

absorbance. This is because MoS₂ with black color has strong optical absorption in the visible light region. The separation/recombination rates of the photo-excited electron-hole pairs of the samples were next investigated by PL spectra. As shown in Fig. 6b, a strong PL emission peak can be observed for the pristine PyP due to the radiative recombination of charge carriers. The PL quenching in these MoS₂/PyP (IM) samples occurs in a saturated emission at 534 nm. It is attributed to the efficient charge transfer at the photoactive MoS₂/PyP(IM) interface and further improved the separation efficiency of the photo-generated charge carriers.

There is one signal Lorentzian line of EPR spectrum centered at a g-factor value of 2.0032 were detected for PyP and MoS₂/PyP(IM) respectively, indicating an unpaired electron on the π -conjugated PyP aromatic rings (Fig. 7a). Compared with pure PyP, the Lorentzian line of MoS₂/PyP(IM) samples was enhanced obviously, presumably because of the redistribution of π -electrons within the hybrid by band offsets. Thus, the heterostructure is beneficial to optimize the electronic band structure for charge migration and separation. The EPR signals of

both PyP and MoS₂/PyP(IM) samples were further increased under visible light irradiation illustrating the generation of unpaired electrons on the π -conjugated aromatic rings and efficient photo-induced generation of charge carrier pairs.

Electrochemical impedance spectra (EIS) were carried out to follow the charge separation and transfer efficiency of photogenerated electrons and holes in the well-developed MoS₂/PyP(IM) material using a typical three-electrode cell. As shown in Fig. 7b, polarization curves recorded with the MoS₂ optimized PyP on FTO glass showed a smaller overpotential for the HER than pure PyP, which benefits by more active edge sites and the electrons trapped by MoS₂ nanosheets are easier to react with H⁺ to produce H₂. Electrochemical impedance spectroscopy displayed in Fig. 7c indicates the charge transfer rate in the dark. Obviously, MoS₂/PyP(IM) shows a smaller arc radius and a lower resistance in charge transportation than that of pure PyP, which is benefited for superior charge separation of photogenerated e⁻-h⁺ pairs. Fig. 7d showed prompt transient photocurrent response of the samples. After decorating PyP with MoS₂, the increased photocurrent response reflect that photoinduced e⁻-h⁺ pairs are separated more efficiently, further indicating the efficient transfer of charge carriers. The increase of photocurrent is also due to the enhanced visible light absorption of MoS₂/PyP(IM). Therefore, we can conclude that construction of MoS₂/PyP(IM) has improved photocatalytic-water-reduction kinetics compared to the pristine PyP and a better photocatalytic performance can be expected.

From the above analysis, a possible photocatalytic mechanism of the samples in HER is proposed briefly. Under visible light irradiation, the excited electrons generated on conduction band of PyP could rapidly transfer to MoS₂ with plenty of active sites. Meanwhile the holes generated at valence band of PyP would quickly move in a different direction and could be trapped by methanol (Scheme 1). On the one hand, the construction of the MoS₂/PyP heterojunction can significantly restrain the charge recombination; on the other hand, MoS₂ as an electron receiver features plenty of active sites for HER thus improves the proton

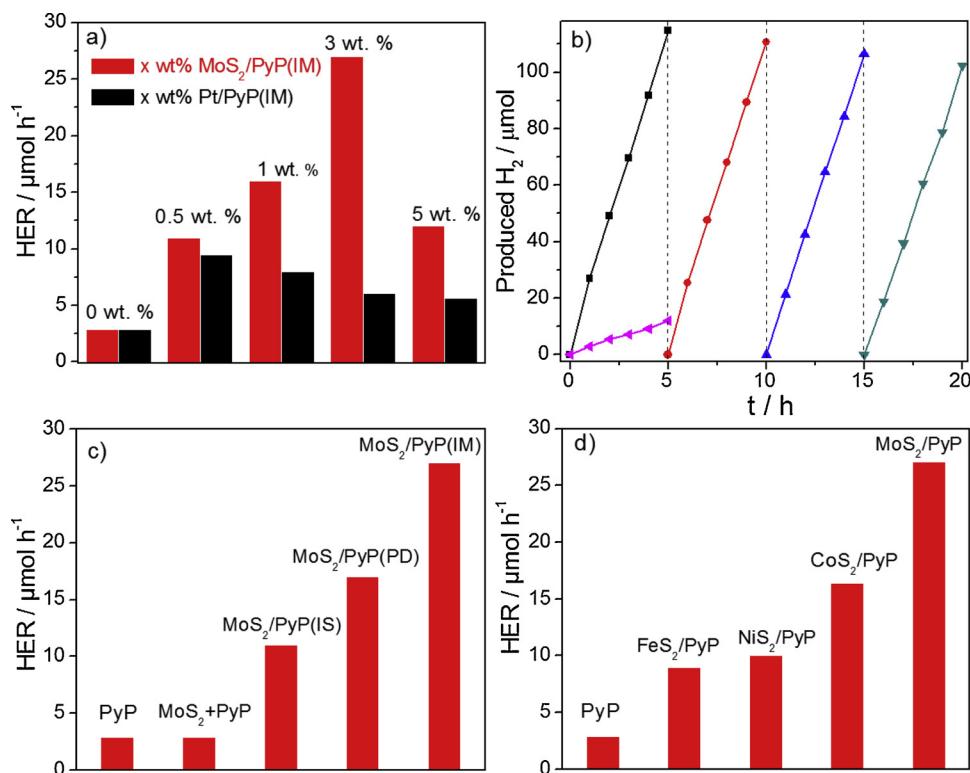


Fig. 8. Photocatalytic H_2 evolution curves ($\lambda \geq 420 \text{ nm}$) of a) $x \text{ wt\% MoS}_2/\text{PyP(IM)}$ samples; b) Stability test of H_2 evolution (evacuation every 5 h) for 3 wt. % $\text{MoS}_2/\text{PyP(IM)}$ samples; c) 3 wt. % MoS_2/PyP samples by different synthesis method; d) 3 wt. % $\text{MS}_2/\text{PyP(IM)}$ samples produced by immersion.

reduction process.

3.2. Photocatalytic performance

Finally, the photocatalytic H_2 production activity on $x \text{ wt\% MoS}_2/\text{PyP(IM)}$ composites were evaluated under xenon arc lamp irradiation using methanol as a scavenger (Fig. 8a). Pristine PyP shows mild photocatalytic activity because of the rapid recombination of photo-generated carrier and few active sites. The introduction of layered MoS_2 makes a significant improvement of PyP in photocatalytic water splitting to H_2 . Fig. 8a shows a typical volcano relationship between hydrogen-evolution-activity and loading contents. Firstly, gradual increase in the hydrogen evolution rate takes place when the incorporation amounts of MoS_2 were increased from 0.5 wt. % to 3 wt. %. The optimum hydrogen-evolution rate over 3.0 wt. % $\text{MoS}_2/\text{PyP(IM)}$ reaches $27 \mu\text{mol h}^{-1}$. The photocatalytic activity of samples decreased while further increasing the amount of MoS_2 in the PyP because of the shading effects that seriously block the incident light absorption of PyP [35,21c]. In addition, when the MoS_2 alone under the experimental conditions, no appreciable H_2 was detected, suggesting that MoS_2 is incapable acted as a photocatalyst for photocatalytic H_2 production. This result further confirms that the improved photocatalytic performance was profited from the construction of MoS_2/PyP heterostructure. Compared with traditional cocatalyst Pt, the optimum hydrogen evolution rate over $\text{MoS}_2/\text{PyP(IM)}$ reaches $27 \mu\text{mol h}^{-1}$ which is ~3-time higher than that of Pt/PyP. This result reveals that the construction of MoS_2/PyP heterojunction has a good performance than that of noble metal Pt in photocatalytic water reduction.

Fig. 8b shows prolonged irradiation with visible light for four cycles lasting 20 h (5 h per cycle). The hydrogen evolution rate of the catalyst did not show evident decrease in the activity, indicating its high stability during photocatalytic H_2 evolution [27c]. The total amount of H_2 in the first cycle was $115 \mu\text{mol}$, much more than that of pure PyP ($12 \mu\text{mol}$). For comparison, Fig. 8c shows the photocatalytic hydrogen

evolution over the optimal $\text{MoS}_2/\text{PyP(IS)}$, $\text{MoS}_2/\text{PyP(PD)}$ and MoS_2+PyP synthesized via the widely reported methods including in-situ, photodeposition and physical mixing. The modification of MoS_2/PyP by different methods (IS or PD) displays further improved photoactivity for H_2 evolution, while MoS_2+PyP physical mixture shows no increase in the activity. The hydrogen evolution rate of 3 wt. % $\text{MoS}_2/\text{PyP(IS)}$ and $\text{MoS}_2/\text{PyP(PD)}$ is 11 and $17 \mu\text{mol h}^{-1}$, respectively, while that of $\text{MoS}_2/\text{PyP(IM)}$ is $27 \mu\text{mol h}^{-1}$. The result implies that the immersion method is more beneficial than the other two fabrication technique (in-situ and photodeposition) in loading MoS_2 onto the PyP for the photocatalytic water splitting to H_2 . The effect of other transition metal sulfides (FeS_2 , CoS_2 , NiS_2) for PyP are also measured for the comparison. Results in Fig. 8d reveal that all the as-prepared composites show good photocatalytic H_2 production activities, while the optimum activity was achieved when MoS_2 was used to construct the heterojunction. This is mainly ascribed to the layered structure of MoS_2 superior to the blocky of other MS_2 which means the layered MoS_2 can greatly matched with PyP, facilitating charge transfer and finally shows the optimum activity. However, the varying degrees of improvement revealed that the construction of heterojunctions by transition metal sulfides with PyP (MS_2/PyP) can efficiently facilitate the H_2 production process.

4. Conclusion

In summary, the well-developed MS_2/PyP heterojunctions by different fabrication techniques (immersion, photodeposition and in-situ methods) and various transition metal sulfides (MoS_2 , FeS_2 , CoS_2 , NiS_2) can serve as efficient photocatalysts for H_2 production. Characterization revealed that the successful construction of heterojunctions can efficiently suppress charge recombination, improve interfacial charge transfer, and provide more active adsorption sites and photocatalytic reaction centers. This study attests the PyP with π -conjugated group used for photocatalytic H_2 evolution is therefore of great significance.

We believe a timely study of the pyrene-based conjugated polymers as emerging heterogeneous photocatalysts would stimulate the investigations for other photocatalytic applications, such as CO₂ reduction, phenol synthesis from benzene, and the selective oxidation of aromatic alcohols.

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